

REPORT

CD NO

DATE OF INFORMATION 1951
DATE DIST. 1 Aug 1952

NO. OF PAGES 5

SUPPLEMENT TO
REPORT

STAT

50X1-HUM

THIS DOCUMENT CONTAINS INFORMATION AFFECTING THE NATIONAL DEFENSES OF THE UNITED STATES WITHIN THE MEANING OF ESPIONAGE ACT 50 U. S. C. 31 AND 32, AS AMENDED. ITS TRANSMISSION OR THE REVELATION OF ITS CONTENTS IN ANY MANNER TO AN UNAUTHORIZED PERSON IS PROHIBITED BY LAW. REPRODUCTION OF THIS FORM IS PROHIBITED.

THIS IS UNEVALUATED INFORMATION

SOURCE Doklady Akademii Nauk SSSR, Vol LXXX, No 4, 1951, p 611-613.

THE CONNECTION BETWEEN ELECTRIC CONDUCTIVITY
AND ACTIVITY OF CATALYSTS IN ALKYLATION REACTIONS

Acad A. V. Topchiyev, Ya. M. Paushkin,
T. P. Vishnyakova, M. V. Kurashov

[Tables and figure referred to are appended.]

In our previous article (1), we proved that there is in general no connection between electric conductivity and, consequently, between ion concentration of the catalyst and catalyst activity. This idea repudiates the theory of the protonic-ionic mechanism under participation of a carbonium ion in alkylation and polymerization reactions.

In this report, the investigation of catalysts was continued, and the change of electric conductivity of catalysts in the alkylation process was studied.

Table 1 presents the authors' determinations of electric conductivity values at various temperatures of a number of new fluorine catalysts and acids frequently used in alkylation reactions and studied in our reports (2,3) and those of other authors (4). The electric conductivity was determined by the customary method, as described in (1).

The data of Table 1 shows that after saturation of the acids with boron fluoride, their electric conductivity decreases, while, at the same time, their catalytic activity increases. Thus, orthophosphoric acid will not cause alkylation of isoparaffins by olefins, while the molecular compound of orthophosphoric acid with boron fluoride $H_3PO_4 \cdot BF_3$ is an active catalyst for the alkylation of isobutane by ethylene, propene, and butene (2).

At the same time, the electric conductivity of the molecular compound is almost ten times lower than that of orthophosphoric acid.

- 1 -

CLASSIFICATION

FOR OFFICIAL USE ONLY

[illegible]

STAT

Sulfuric acid apparently does not form a molecular compound with boron fluoride, but a saturated solution of BF_3 in concentrated (94-100%) H_2SO_4 is a more active catalyst than the initial H_2SO_4 . Thus, sulfuric acid does not cause the alkylation of benzene by ethylene, while a boron fluoride solution in sulfuric acid will assist the reaction.

It was interesting to clear up how the specific electric conductivity of the catalysts changes in the process of the alkylation reaction in relation to the loss of activity by the catalyst.

For this purpose, the electric conductivity and the other properties of the catalysts $\text{H}_3\text{PO}_4 \cdot \text{BF}_3$ and H_2SO_4 in the alkylation of benzene and isopentane by olefins were measured. Benzene with 80 - 81° C bp and $d_4^{20} = 0.881$ sp gr was used. The propene was obtained by dehydrogenation of isopropyl alcohol (82-83° C bp) and contained 99% unsaturated compounds. The catalyst had the composition $\text{H}_3\text{PO}_4 \cdot \text{BF}_3$ with $d_4^{20} = 1.90$ sp gr.

A number of successive experiments was carried out. After each experiment the electrical conductivity was determined. In each experiment, 200 ml of benzene, 30.5 liters of propene (molar ratio $\text{C}_3\text{H}_6 : \text{C}_6\text{H}_6 = 1 : 1.75$), and 25 ml of catalyst were used. The propene was admitted under energetic stirring at a rate of 1-1.5 liters/hr. After each experiment, the electric conductivity of the catalyst was determined at 25° C; the alkylate was distilled in a rectification column to yield the following fractions: the 0-120° C fraction, containing mostly the benzene which had not entered into the reaction; the 120-170° C fraction, called the alkylate (containing isopropyl benzene); and a residue boiling above 170° C.

In most of the experiments, the alkylate (i.e., the fraction with a plus-120° C bp) contained 75-80% of isopropyl benzene which distilled over in the range of 145-155° C and had $d_4^{20} = 0.8630$ sp gr.

The experiments with the same batch of catalyst (25 ml) lasted 40 da. In the course of this period, 153 liters of propene were admitted and 635 g of alkylate were obtained.

In the process of the reaction, the activity of the acid catalyst decreases due to the formation of acidic esters from propene and the acid and due to the saturation of the catalyst by resins. In this process, the catalyst concentration is lowered, which is indicated by a drop in the specific gravity and a parallel drop in electric conductivity. At the moment at which the catalyst loses activity, which can be judged by the yield of alkylate, its specific gravity and electric conductivity drop sharply. Figure 1 gives a graphic representation of this dependence.

Analogous experiments on the investigation of electric conductivity were carried out with 98.5% H_2SO_4 as catalyst in the alkylation of isopentane by isobutene. A quantity of 5 liters of isobutene (obtained by the dehydrogenation of isobutyl alcohol) was passed at 10° C and at a rate of 1-1.5 liters/hr through 50 ml isopentane (27.3° C bp) which were mixed energetically with 30 ml of sulfuric acid. Ten consecutive experiments were carried out with the same 30-ml batch of catalyst, and 50 liters of isobutene were admitted. As a result, 236 ml of alkylate were obtained. After distilling off the isopentane in a rectification column up to 30° C, alkylate with a 30-170° C bp range and a residue boiling above 170° C were collected.

Table 3 shows the results of the experiments.

STAT

✓ In these experiments, too, the specific gravity, electric conductivity and ~~of~~ sulfuric acid were lowered due to the formation of acidic volumetrically determined acidity resulting from the presence of esters by the sulfuric acid, parallel to lowering of the catalyst activity, which could be estimated from the yield of the alkylate.

After the fourth experiment, when the concentration of the H_2SO_4 had dropped below 85% the yield dropped sharply and polymerization was chiefly found to occur. This could be seen from the increase of the heavy residue with a plus-170° C bp which was rich in polymers. In this stage of isobutene polymerization, the electric conductivity of the catalyst was also lowered.

We demonstrated in this manner that the specific electric conductivity of a specific catalyst can serve as a convenient characteristic of the activity of this catalyst, because in proportion to the lowering of the activity in the reaction process, the catalyst is diluted by such substances as acidic esters and resins which have lower electric conductivity. Lowering of the concentration of the electrolyte by anhydrous solvents lowers the electric conductivity.

This does not contradict our general conclusion (1) that the electric conductivity taken for different catalysts (e.g., H_2SO_4 and $H_3PO_4 \cdot BF_3$) cannot serve as a characteristic of their relative activity, as there is no over-all parallelism between these two factors.

BIBLIOGRAPHY

1. A. V. Topchiyev, Ya. M. Paushkin, T. P. Vishnyakov, M. V. Kurashov, Doklady Akademii Nauk SSSR, Vol LXXX, No 3, 1951
2. A. V. Topchiyev, Ya. M. Paushkin, Uspekhi Khimii, Vol VI, p 664, 1947
3. A. V. Topchiyev, Ya. M. Paushkin, Soyedineniya Fluoristogo Bora Kak Katalizatory u Reaktsiyakh Alkilirouaniya, Polimerizatsii, i Kondensatsii (Boron Fluoride Compounds as Catalysts for Alkylation, Polymerization, and Condensation Reactions), Moscow, 1949
4. H. S. Booth, D. R. Martin, Boron Trifluoride and Its Derivatives, New York; London, 1949

✓ Appended tables and figure follow.7

Table 1. Specific Electric Conductivity of a Number of Acid Catalysts

Temp ° C	Specific Conductivity, ohm ⁻¹ cm ⁻¹			
	H_2SO_4 (100.1%)	H_2SO_4 (100.1%) + BF_3	$H_3PO_4 \cdot BF_3$	H_3PO_4
0	--	--	1.003207	--
5	0.022005	1.017147	0.004357	--
10	0.029177	0.020119	0.004692	--
15	--	0.025290	0.005209	--
20	0.033685	0.027058	0.005834	--
25	0.043595	0.035694	0.007227	0.0510
30	0.049742	0.041639	0.008148	--

STAT

Table 2. Change of the Properties of $H_3PO_4 \cdot BF_3$ Catalyst
in Alkylation of Benzene With Propene

No of Experi- ments	Yield of Alkylate In % Re- ferred to Propene (bp > 120° C)	Consumption of Catalyst in % Referred to Alkylate	d_4^{20} of Catalyst	Specific Electric Conductivity of Cat. yst in $ohm^{-1}cm^{-1}$
0	--	--	1.900	0.0071
1	186	46.2	1.823	0.00647
2	220	21.4	1.816	0.00627
3	236	13.9	1.812	0.00618
4	269	9.9	1.625	0.00535
5	130	8.5	1.331	0.00058

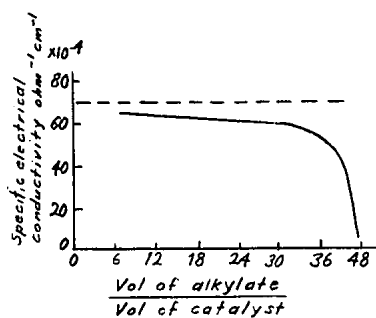


Figure 1. Dependence of Alkylate Yield on
Electrical Conductivity of Catalyst

Table 3. Change of the Properties of H_2SO_4 Catalyst
in Alkylation of Isopentane With Isobutene

No of Experiments	Yield of Alkylate in % Referred to Isobutene		d_4^{20} of Alkylate	Consumption of Catalyst in % Referred to Alkylate	d_4^{20} of Catalyst	Concentration of Catalyst in %	Specific Electrical Conductivity of Catalyst in $ohm^{-1} cm^{-1}$
	(30-170 C)	(Above 170 C)					
0	--	--	--	0	1.8420	98.3	0.1150
3	183	23	0.708	209.5	1.7660	90.0	0.1000
4	162	58	0.710	85.0	1.7342	86.9	0.0930
6	62.6	82	0.729	83.7	1.6903	83.7	0.0674
8	20	105	0.746	53.2	1.5259	62.6	0.0341
10	12.5	42	0.760	51	1.4190	60.6	0.0233

- END -
- 5 -

STAT